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MULTIVARIATE STATISTICAL APPROACHES TO IDENTIFY HEAVY METAL SOURCES IN ULAANBAATAR SOIL

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ABSTRACT

Soil contamination with heavy metal is a serious environmental problem due to its impact on human health. The existence of heavy metals in soils is attributed to both anthropogenic and lithogenic factors. In the present work, 58 soil samples were collected from Ulaanbaatar to assess the potential for contamination and potential availability of some heavy metals (Co, Cr, Ni, Mn, Cu, Pb, Cd and Zn) and to identify possible contribution sources of heavy metals by means of multivariate statistical analysis. The factor analysis and cluster analysis revealed that Co, Ni and Mn are lithogenic factor, while Cu, Pb, Zn are defined as anthropogenic input with similar pollution sources and Cd exhibits both natural and anthropogenic sources. Cr is not correlated with other elements, attributing to anthropogenic factor controlled by local source. The higher amount of releasable form was found for elements: Co >Pb >Ni > Zn >Cu >Cr >30%, in contract to that the higher amount of mobile form was found for elements: Cd >Mn >10%. This result can be associated with loss of natural properties of Ulaanbaatar soil.

KEYWORDS: Species, Principal Component Analysis, Surface Soil, Ulaanbaatar

INTRODUCTION

Soil contamination with heavy metal is a serious environmental problem due to its impact on human health [1-4]. The existence of heavy metals in soils is attributed to both anthropogenic and lithogenic factors. The Cd, Cr, Pb, Zn and Cu are the most frequently reported heavy metals due to their potential hazards in environment [5, 6]. Last two decades, the surface soil contamination of Ulaanbaatar with heavy metal has attracted a serious attention due to the high-density of urbanization caused by massive migration of rural residents to city. The Ulaanbaatar soil is heavily polluted by the traffic and industrial emission, coal combustion in “Ger” region and dusts from building materials. However, there are quite a few studies of Ulaanbaatar pollution with heavy metals [7, 8].

The main contributions of the present study are (i) to assess total concentration and potential availability of some heavy metals (Co, Cr, Ni, Mn, Cu, Pb, Cd and Zn) in Ulaanbaatar soil and (ii) to identify possible sources contribution of heavy metals by means of multivariate statistical analysis. Multivariate analysis such as factor analysis has been widely used to identify the natural and anthropogenic contribution of heavy metal and possible pollution sources. These techniques are based on the reduction of the data set by obtaining possible relationships between the variables (concentration of the metals) give complementary information in different forms. Factor Analysis (FA) groups correlated variables, generating a new set of variables called Principal Components (PCs). Hierarchical Cluster Analysis (HCA) examines the similarities between the variables in a data set and the derived result is usually represented in the

dendrogram.

The heavy metals in urban soil are usually characterized by non-Gaussian (normal) distribution mainly due to their anthropogenic inputs. In that case, the raw data sets has to be normalized prior to multivariate statistical analysis to avoid result distortions and low levels of significance. The choice of transformation power for normalization depends on the distortion degree from normality. The Box-Cox transformation is the most powerful transformation method for data set with too high skewness and outliers.

SOIL SAMPLING AND ANALYSIS

The location of sampling points of 58 soil samples (at a depth of 0-10 cm) collected in 2010 are shown in the Figure 1. Soil samples were dried at room temperature, homogenized and manually removed the large inclusions such as stones, glass, plant roots, then sieved to 2 mm with stainless steel mesh and grounded on the laboratory vibration mill-disk “Pulverisette 9”, Fritsch.

Figure 1: The Location of Soil Samples Collected from Ulaanbaatar City. (□- Vegetated Area, Δ- Next to Power Plants, O –in the “ger” Area, x- Along Road Way)

Total concentrations of heavy metals (Mn, Ni, Co, Cr, Cu, Cd, Zn, Pb) were determined by arc atomic emission spectrometry. The evaluation of potential availability of heavy metals was performed using two single extractions of 2M HNO_3 and buffer solution NH_4-Ac (pH 4.8). The heavy metal concentration in the obtained solutions were determined by flame atomic absorption spectrophotometer (Perkin-Elmer 5000) and inductively coupled plasma-atomic emission spectrometry ICP-AES (iCAP 6300 Duo Scientific, USA), respectively.

Descriptive statistical analysis was conducted as a first step towards an elementary understanding of concentrations of elements. The multivariate statistical techniques (factor analysis and hierarchical cluster analysis) were applied to total concentration of heavy metals to identify possible contribution sources. Box-Cox transformation [9] was carried out on raw data sets prior to multivariate statistical analysis to avoid result distortions and low levels of significance.

RESULTS AND DISCUSSIONS

The Heavy Metal Concentrations: Total concentration of heavy metals was used to evaluate the potential for contamination and to identify the pollution source and. The pollution index and the percentage of the number of samples exceeding the regional background values were obtained to assess the potential for contamination. The pollution index was calculated in relation to the region background values [10]. The descriptive statistics of heavy metals concentrations, regional background value and maximum permissible concentration according to standard in Mongolia [11] were presented in the Table 1.

Table 1: The Range, Mean and Median of the Total Concentration of Heavy Metals (mg/kg), background value (BG, mg/kg), maximum Permissible Concentration (MPC, mg/kg), Pollution index (PI) and Percentage of Number of Samples Exceeding the BG (n, %)

n=58	Min.	Max.	Mean	Median	BG [10]	PI	n, %	MPC [11]
Co	4.80	19.00	12.26	12.00	18	0.67	5	30-40
Mn	250.00	920.00	639.31	660.00	710	0.93	28	NA
Ni	15.32	59.49	33.23	32.00	33	0.97	47	60-100
Cr	30.00	105.00	51.00	48.50	45	**1.08**	64	60-100
Cd	0.41	2.90	0.95	0.73	1	0.73	21	3.00
Zn	72.00	640.00	138.36	120.00	60	**2.00**	100	**50-100**
Pb	19.00	1370.00	93.12	45.50	20	**2.28**	95	50-70
Cu	20.00	1400.00	68.66	41.00	25	**1.64**	97	60-80

NA -not available

The significant differences between mean and median having wide range was found for Cu, Pb, Zn, Cr, Cd elements. These elements also show high pollution index. Due to their wide range distribution, we consider only the median values for future analysis. The medians of the heavy metal concentration are increased in the following order: Cd< Co< Ni< Cu< Pb< Cr < Zn< Mn, while their pollution indexes are increased in the following order: Co< Cd< Mn< Ni< Cr< Cu< Zn< Pb. The medians of Co, Cd, Mn, Ni are found lower than background value, where the 5, 21, 28, 48% of the soil samples exceed their background levels, respectively. The pollution index of the rest elements is found in the range of 1.08 - 2.28, where more than 64% of samples exceed their background levels. In the present study, all heavy metal concentrations except Zn are found lower than maximum permissible concentration (MPC).

Data Distribution and Transformation: The frequency distributions of the total concentration of heavy metals and their normal (Gaussian) fittings are presented in the Figure 2. It can be clearly seen that Co, Mn and Ni exhibits unimodal distribution, while Cr, Cd, Cu, Zn and Pb exhibit bimodal distribution with outliers at high end. The some higher values of Cr around 90-110 mg/kg are found in the industrial region and high-traffic crossword. The soil sample#30 taken from the "ger" region along the traffic road showed the extreme higher content of Cu (1400 mg/kg), Zn (640 mg/kg) and Pb (1370 mg/kg). The soil sample#58 taken from the "ger" region has extreme higher content only for Pb (1300 mg/kg).

The parameters of skewness, kurtosis and p-value of Shapiro-Wilk test for normality performed on total concentration of heavy metals are shown Table 2. The higher values of skewness and kurtosis of Cr, Cd, Cu, Zn, Pb distributions are mainly due to the presence of the extremely high values or outliers shown in the Figure 2. In addition, Shapiro-Wilk (S-W $p>0.05$) test for normality results that the only Co, Ni, Mn have Gaussian distribution.

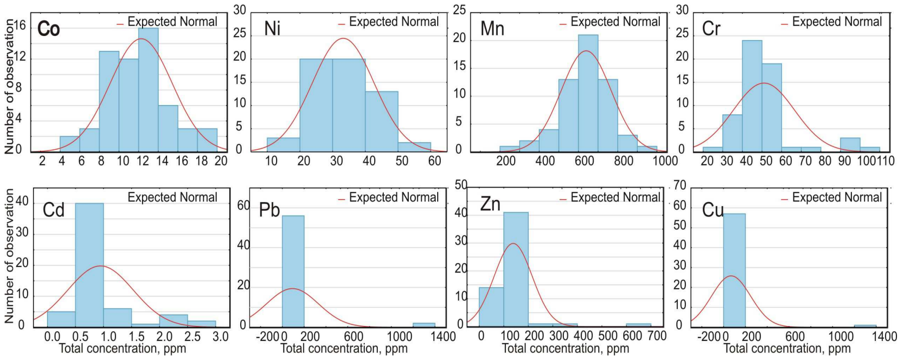

Figure 2: Frequency Histogram of Total Concentration Fitted with Gaussian Distribution

Table 2: Skewness, Kurtosis and Significance Level of Shapiro-Wilk (S-W, p) Test for Normality of Raw and Transformed Data Sets of Total Concentration

	raw data			Box-Cox transformed		
	Skewness	Kurtosis	S-W,p	Skewness	Kurtosis	S-W, p
Co	0.05	0.19	0.30	0.01	0.21	0.31
Ni	0.34	-0.20	0.56	-0.02	-0.36	0.90
Mn	-0.49	0.57	0.47	-0.02	0.02	0.97
Cr	1.95	4.46	0.00	-0.04	0.72	0.04
Cd	2.06	3.49	0.00	0.09	-0.16	0.38
Zn	5.12	31.71	0.00	-0.07	0.70	0.29
Pb	5.16	25.82	0.00	0.02	0.24	0.57
Cu	7.45	56.19	0.00	-0.11	1.81	0.10

Box-Cox transformation was carried out on raw data sets prior to multivariate statistical analysis to avoid result distortions and low levels of significance of heavy metals especially in case of Cu, Cd, Zn, Pb and Cr. The parameters of transformed data sets and their frequency histograms with Gaussian fittings are given in the Table 2 and Figure 3, respectively. Box-Cox transformed data sets exhibit much lower values of skewness and kurtosis than raw data sets resulting in good fitting with Gaussian. Shapiro-Wilk (S-W $p>0.05$) test for normality passed for all elements except Cr.

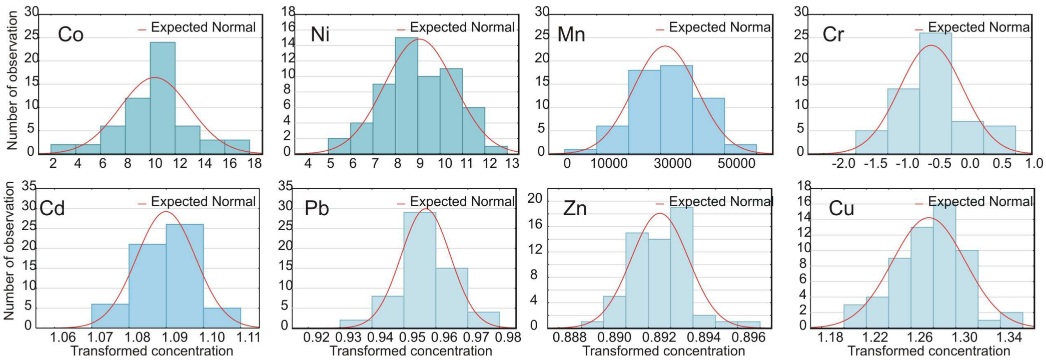

Figure 3: Frequency Histogram of Box-Cox Transformed Data Sets Fitted with Gaussian Distribution Multivariate Statistical Analysis

The Person's correlation was performed on the transformed data sets of total concentration of heavy metals (Co, Mn, Ni, Cd, Cr, Cu, Pb and Zn). The obtained correlation coefficients given in the Table 3 show that more significant correlations exhibit between Co, Mn and Ni ($r_{Co,Mn}$ = 0.701, $r_{Ni,Co}$ = 0.552, $r_{Ni,Mn}$=0.475), and Pb, Cu and Zn ($r_{Pb,Cu}$ =0.635, $r_{Pb,Zn}$=0.572, $r_{Zn,Cu}$=0.471). Cd is correlated with Cu and Co ($r_{Cd,Cu}$= 0.546, $r_{Cd,Co}$= 0.475), while the only Cr is not correlated with any of these elements.

Table 3: Person's Correlation Coefficients of the Total Concentration of Heavy Metal

	Co	Mn	Ni	Cd	Cr	Cu	Zn	Pb
Co	1	**0.701**	**0.522**	*0.475*	-0.058	0.155	-0.209	-0.036
Mn	**0.701**	1	*0.436*	0.162	-0.298	0.043	-0.432	-0.119
Ni	**0.522**	*0.436*	1	0.252	0.156	0.312	0.059	0.133
Cd	*0.475*	0.162	0.252	1	0.068	**0.546**	0.134	0.238
Cr	-0.058	-0.298	0.156	0.068	1	0.108	0.106	-0.018
Cu	0.155	0.043	0.312	**0.546**	0.108	1	*0.471*	**0.635**
Zn	-0.209	*-0.432*	0.059	0.134	0.106	*0.471*	1	**0.572**
Pb	-0.036	-0.119	0.133	0.238	-0.018	**0.635**	**0.572**	1

Table 4: Total Variance and Rotated Factor Loading

	PC1	PC2	PC3
Co	**0.899**	-0.061	-0.082
Mn	**0.790**	-0.251	-0.392
Ni	**0.728**	0.149	0.245
Cd	**0.565**	**0.449**	0.101
Cr	0.010	0.010	**0.964**
Cu	0.319	**0.826**	0.084
Zn	-0.257	**0.796**	0.144
Pb	-0.001	**0.864**	-0.110
% Var.	32.2	28.9	13.8

In this work, multivariate statistical analysis such as factor analysis and cluster analysis were employed to identify the natural or anthropogenic contributions. The factor analysis (varmax rotation of covariance matrix) revealed three factors (an eigenvalue >1) with a cumulative variance of 84.9% (Table 2).

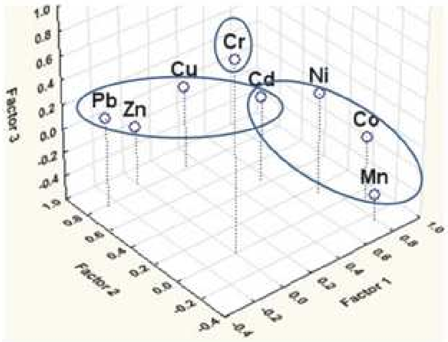

Figure 4: The Spatial Representation of Three Rotated Components PC1, PC2 and PC3

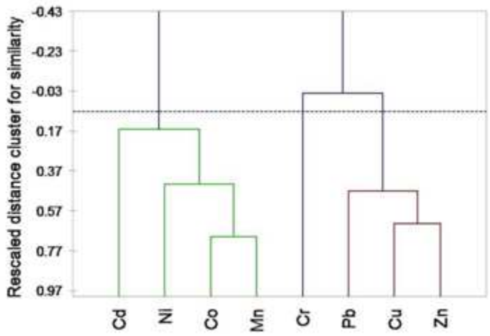

Figure 5: The Results of Cluster Analysis

The first principal component (PC1) explaining 32.2 % of the total variation, exhibited a high positive factor loading on Co, Mn, Ni and partially positive factor loading on Cd. The PC2 explaining 28.9 % of total variance, exhibited a high positive factor loading on Cu, Pb, Zn and partially positive factor loading on Cd. The PC3 explaining 13.8 % of the total variation, exhibited a high positive factor loading on Cr. The representation of three factor loadings is shown in the Figure 4. Co, Ni and Mn in the first principal component, having a high positive loading factor of >0.728 can be defined as natural factor of lithogenic process during weathering progress of natural parent material in the soil. This finding can be confirmed by their lower pollution index (less than one) and Gaussian distribution. In the second principal component, Cu, Pb, Zn with a high positive loading of >0.796 can be defined as anthropogenic input with similar pollution sources such as traffic and domestic emissions. The results can be confirmed by their higher pollution index and higher percentage of soil

samples exceeding the background value. In addition, heterogenic distribution of these elements with higher skewness and kurtosis are likely associated with their anthropogenic input in the soil. Cd exhibits partially loading factor on both PC1 and PC2, indicating its natural and anthropogenic sources. In the third principal component, Cr, which is not correlated with other elements, may be controlled by local source. In fact, that Cr exhibits highly heterogenic spatial distribution, which does not pass Box-Cox transformation.

Cluster analysis is widely used in addition to factor analysis, since they give complementary information in the different forms. The results hierarchical cluster analysis was consistent with that of factor analysis. The derived dendrogram show three group clusters. The first cluster includes Mn, Co, Ni and Cd indicating their lithogenic sources. The second cluster includes Zn, Cu and Pb indicating their anthropogenic contribution with similar pollution sources, which likely caused by emission of power plant, traffic infrastructure and coal combustion in “ger” region. Cr in the third cluster latter combined with second cluster indicating its anthropogenic input with local pollution sources.

Heavy Metal Potential Availability: In present study, the potential availability of heavy metals focused on the two forms. The releasable form obtained with the extraction of 2M HNO_3. The fraction of heavy metals, which is not dissolved in 2M HNO_3 considered to be to associated with parent minerals (primary silicates), thus it is more stable under environmental condition. Therefore, heavy metal in the dissolved fraction can be mobilized under specific environmental conditions (pH and redox potential). The mobile form obtained with the extraction of buffer solution NH_4-Ac (pH 4.8) is readily available to environment such as water and plants. The concentrations of releasable and mobile forms were expressed as percentages in the different fractions with respect to the total amount of heavy metals in the soil. The results are given in the Table 5.

Table 5: Heavy Metal Potential Availability given in Percentage of the Total Metal Content

form availability	Co	Pb	Ni	Zn	Cu	Cr	Mn	Cd
releasable (%)	**61.98**	**56.18**	**53.14**	**49.96**	**42.33**	**32.94**	23.42	13.79
mobile (%)	4.33	4.40	2.98	6.17	2.17	2.06	**12.95**	**27.59**

The present result shows that the higher amount of releasable form was found for elements: Co >Pb >Ni > Zn >Cu >Cr >30%, in contract to that higher amount of mobile form was found for elements: Cd >Mn >10%. The inverse correlation between releasable and mobile forms can be associated with loss of natural properties of Ulaanbaatar soil.

CONCLUSIONS

The total concentration and potential availability of some heavy metals (Co, Cr, Ni, Mn, Cu, Pb, Cd and Zn) in 58 samples collected from soils in Ulaanbaatar were determined. The higher amount of releasable form was found for elements: Co >Pb >Ni > Zn >Cu >Cr >30%, in contract to that higher amount of mobile form was found for elements: Cd >Mn >10%. The inverse correlation between releasable and mobile forms can be associated with loss of natural properties of Ulaanbaatar soil.

The multivariate statistical analysis was applied to identify possible contribution sources of heavy metals. The factor analysis and cluster analysis revealed that Co, Ni and Mn are defined as natural factor of lithogenic process, while Cu, Pb, Zn are defined as anthropogenic input with pollution sources, Cd exhibits both natural and anthropogenic sources. Cr is not correlated with other elements indicating anthropogenic factor controlled by local source.

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